

# A fluctuation relation for weakly ergodic aging systems

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(Dated: \$ V 13.3.0 2012/08/13 10:37 AC \$)

A fluctuation relation for aging systems is introduced, and verified by extensive numerical simulations. It is based on the hypothesis of partial equilibration over phase space regions in a scenario of entropy-driven relaxation. The relation provides a simple alternative method, amenable of experimental implementation, to measure replica symmetry breaking parameters in aging systems. The connection with the effective temperatures obtained from the fluctuation-dissipation theorem is discussed.

PACS numbers: 05.40.-a, 05.70.Ln

Non-equilibrium systems are characterized by a net energy transfer (in the form of work, heat, or mass) to the environment. Aging systems pertain to the category of weakly ergodic non-equilibrium systems [1, 2] exhibiting slow relaxational dynamics and strong history dependent effects where the fluctuation-dissipation theorem (FDT) is violated [3–6]. This has led to the introduction of the concept of non-equilibrium or effective temperature [7]. Despite of the insight gained from exactly solvable models and other conceptual attempts (e.g. [8, 9]) we still lack a clear understanding of the general picture describing aging systems. In contrast to stationary systems, aging systems are described by two timescales: the waiting time  $t_w$  elapsed since the system was set in the non-equilibrium state and the time  $t > t_w$  at which measurements are taken. A characterization of the full spectrum of fluctuations appears key for a satisfactory understanding of the aging state.

Over the past years several results about energy fluctuations in non-equilibrium states have been obtained under the heading of fluctuation theorems (FTs) [10, 11]. FTs take slightly different mathematical forms depending on the specific non-equilibrium context [12, 13]. However all them share the same common feature: they relate probabilities of absorbing and releasing a given amount of energy under non-equilibrium conditions; they are useful in small systems and short times where energy fluctuations can be directly measured allowing us, for example, to extract free energies of kinetic molecular states from irreversible pulling experiments [14].

In this work we present a theoretical derivation of a fluctuation relation in aging systems. The aging fluctuation relation (AFR) is based on the hypothesis of partial equilibration in a scenario of entropy-driven slow relaxation. It can be written in terms of a phase-space contraction factor  $x$  that bears resemblance to the order parameter  $x(q)$  defined in the context of spin glasses

[15]. The new relation is further supported by extensive numerical simulations. The existence of an AFR was already suggested in Refs. [16, 17] and recently hinted at in a quench experiment of a gelatin droplet that exhibits a sol-gel transition [18]. In that reference heat distributions were measured and shown to satisfy a fluctuation relation for a system in contact with two baths at different temperatures. Yet it remains unclear whether the same relation applies to other aging systems. In contrast, the new relation we are proposing should be generally valid in aging systems and is amenable to future experimental verification in noise measurements of glass formers, critical systems and small systems (e.g. single molecules).

*The aging fluctuation relation (AFR).* Consider a system quenched at time  $t = 0$  from an high-temperature equilibrium state down to temperature  $T$  where it ages exhibiting slow relaxation and activated dynamics phenomena. Such aging state is characterized by low entropy-production rate and loss of time-translational invariance [19]. During the aging process the system continuously exchanges energy with the bath, but some relaxational events result in larger than typical amounts of heat  $Q$  released to the bath, leading to a net positive entropy production  $\langle \Delta S \rangle = \langle Q \rangle / T > 0$ , where the brackets  $\langle (\dots) \rangle$  denote the average over dynamical histories.

To analyze the spectrum of heat or entropy production fluctuations in the aging state we consider the Bochkov-Kuzovlev work fluctuation relation, originally introduced as a generalization of the FDT [20]. After a time  $t_w$ , elapsed since the system was quenched, a constant external perturbation of strength  $h$  coupled to an observable  $A$  is applied to the system. This will cause a change in  $A$  during its subsequent evolution. The entropy production during the time interval  $[t_w, t]$  ( $t \geq t_w$ ) caused by the perturbation is equal to  $\Delta S_{t_w, t} = Q_{t_w, t} / T = h[A(t) - A(t_w)] / T = h\Delta A_{t_w, t} / T$ . This quantity has been

termed exclusive work in [21] and satisfies a fluctuation relation if the system is equilibrated at  $t_w$  (which is not the case here).  $\Delta S_{t_w,t}$  is a fluctuating quantity changing upon repetition of the same experiment. Moreover in the aging regime, where relaxation dynamics is ruled by the complex topological structure of the phase space, made of many almost degenerate metastable states,  $\Delta S_{t_w,t}$  displays a strong intermittent behavior. This means that for fixed  $t_w$  and  $\Delta S$  the requirement  $\Delta S_{t_w,t} = \Delta S$  defines a very broad interval of times  $t$  covering many, well separated, timescales. In such a context a data analysis for fixed  $t_w$  and  $t$  may be ambiguous since it may mix up processes with different timescales, as noticed some years ago in the framework of turbulence [22, 23]. To overcome this problem we define  $P_{t_w}(\Delta S)$  as the probability of observing the value  $\Delta S_{t_w,t} = \Delta S$  after  $t_w$ .

In Ref. [16] a similar approach, based on the concept of Inherent Structure, was used. The idea was to look for  $\Delta S_{t_w,t}$  associated to the first jump out of an Inherent Structure. While this definition could in principle be used in a numerical simulation, it is far less useful in a real experiment. In contrast, the one proposed here is well suited for real experiments.

Despite the fact that the perturbing field  $h$  favors positive values of  $\Delta S_{t_w,t}$ , trajectories with negative values can be observed as well. We argue that, for long enough  $t_w$ , the probability of observing positive and negative values of  $\Delta S$  satisfies the following fluctuation relation (AFR)

$$\log \left[ \frac{P_{t_w}(\Delta S)}{P_{t_w}(-\Delta S)} \right] = x_{t_w} \frac{\Delta S}{k_B}, \quad (1)$$

where  $k_B$  is the Boltzmann constant (equal to 1 in the following). If at  $t_w$  the system is in equilibrium, then  $x_{t_w} = 1$  and Eq. (1) reduces to the Bochkov-Kuzovlev work fluctuation relation [20, 21].

In aging systems, such as glasses, the FDT is not violated for times  $t - t_w \lesssim t_w$  after switching on the perturbation. This is because the degrees of freedom whose characteristic relaxation times are sufficiently smaller than  $t_w$  have equilibrated. In the present context this means that small enough energy transfers between the system and the bath occur in equilibrium, and hence  $x_{t_w} \simeq 1$ . This remains true as long as  $|\Delta S|$  is smaller than a cross-over value  $\Delta S^*$ , which sets the scale of the typical minimum energy transfer in processes that involve non-equilibrated degrees of freedom. For  $|\Delta S| > \Delta S^*$  non-equilibrium energy exchange processes responsible of slow relaxation come into play, and the equality  $x_{t_w} = 1$  is violated. Not all degrees of freedom can contribute to the relaxation process, some of them being frozen at  $t_w$ , and hence  $x_{t_w} < 1$ . As the system ages more degrees of freedom equilibrate at  $t_w$ , and hence  $\Delta S^*$  increases with  $t_w$ . In the limit  $t_w \gg t_{eq}$ , where  $t_{eq}$  is the equilibration time, all degrees of freedom have equilibrated and  $x_{t_w}$  converges to 1 for all  $\Delta S$ . We note that this may not be

the case for mean-field models where metastable states have infinite lifetime.

To justify Eq. (1) we consider a system whose time evolution is ruled by the Langevin equation

$$\frac{d\varphi}{dt} = -\frac{\delta}{\delta\varphi} H(\varphi) + h + \xi \quad (2)$$

where  $\varphi$  is an  $N$ -dimensional field,  $\xi(t)$  a Gaussian white noise (thermal noise) of zero average and correlation  $\langle \xi(t) \xi(t') \rangle = 2T \delta(t - t')$ ,  $-\delta H(\varphi)/\delta\varphi$  the force arising from the conservative energy  $H(\varphi)$ , and  $h$  the constant external field coupled to the macroscopic observable  $\psi_t = \sum_i \varphi_t^i$ , where  $i$  denotes a site index. Fluctuation relations derive from the behavior of the probability  $\mathcal{P}$  of a trajectory  $\{\varphi_s\}_{s \in [t_w, t]}$  and its reverse  $\{\tilde{\varphi}_s\}_{s \in [t_w, t]} \equiv \{\varphi_{t+t_w-s}\}_{s \in [t_w, t]}$ . These can be easily computed using the path integral formalism, see e.g. [24]:

$$e^{-\Delta S_{t_w,t} + \Delta S^{eq}} \mathcal{P}[\{\varphi_s\}_{s \in [t_w, t]}] = \mathcal{P}[\{\tilde{\varphi}_s\}_{s \in [t_w, t]}] \quad (3)$$

where  $\Delta S_{t_w,t} = \beta h(\psi_t - \psi_{t_w})$  and  $\Delta S^{eq} = \beta[H(\varphi_t) - H(\varphi_{t_w})] = -\ln[P^{eq}(\varphi_t)/P^{eq}(\varphi_{t_w})]$ . The quantities in the exponent depend on the trajectory end-points only, then summing over all trajectories from  $\varphi_{t_w}$  at  $t_w$  to  $\varphi_t$  at time  $t$ , and including normalized probability distributions  $P_0(\varphi_{t_w})$  and  $P_1(\tilde{\varphi}_{t_w}) = P_1(\varphi_t)$  for the initial and final states, we get

$$e^{-\Delta S_{tot}} P(\varphi_t, t | \varphi_{t_w}, t_w) P_0(\varphi_{t_w}) = P(\varphi_{t_w}, t | \varphi_t, t_w) P_1(\varphi_t) \quad (4)$$

where  $P(\varphi_t, t | \varphi_{t_w}, t_w)$  and  $P(\varphi_{t_w}, t | \varphi_t, t_w)$  are the conditional probabilities of the forward  $\varphi_{t_w} \rightarrow \varphi_t$  and reverse  $\varphi_t \rightarrow \varphi_{t_w}$  trajectories, respectively, and  $\Delta S_{tot} = \Delta S_{t_w,t} - \Delta S^{eq} + \Delta S_b$ , with  $\Delta S_b = -\ln[P_1(\varphi_t)/P_0(\varphi_{t_w})]$ . From this relation the following identity follows

$$P_{t_w,t}(-\Delta S) = \langle \delta(\Delta S_{t_w,t} - \Delta S) e^{-\Delta S_{tot}} \rangle_{t_w,t} \quad (5)$$

where the average is over the forward process  $\varphi_{t_w} \rightarrow \varphi_t$  with initial probability distribution  $P_0(\varphi_{t_w})$ .

After the quench the system partially equilibrates inside independent phase-space regions (that we will call cages), from which it will escape only after a time  $t - t_w \sim t_w$ . Therefore, when  $t - t_w \ll t_w$  the system is in (partial) equilibrium with the thermal bath,  $P_0(\varphi) = P_1(\varphi) \propto P^{eq}(\varphi)$  so that  $\Delta S^{eq} = \Delta S_b$ ,  $\Delta S_{tot} = \Delta S_{t_w,t}$ , and from (5) one gets eq. (1) with  $x_{t_w} = 1$ .

To study the opposite limit  $t - t_w \gg t_w$ , where the system can access different cages, we observe that  $\Delta S_{t_w,t}$  depends only on the macroscopic variables  $\psi_t$  and  $\psi_{t_w}$ , then the average on the r.h.s of (5) can be done by partial classification, that is by averaging first over all paths with given initial and final states, and then over  $\psi_t$  and  $\psi_{t_w}$ :

$$P_{t_w,t}(-\Delta S) = \int d\psi_{t_w} \int d\psi_t \delta(\Delta S_{t_w,t} - \Delta S) \times \langle e^{-\Delta S_{tot}} \rangle_{\psi_{t_w}, t_w; \psi_t, t} \quad (6)$$

where  $\langle(\dots)\rangle_{\psi_{t_w} t_w; \psi_t t}$  denote dynamical averages restricted to those trajectories starting with  $\psi_{t_w}$  at  $t_w$  and ending with  $\psi_t$  at  $t$ . Assuming the system is partially equilibrated over cages, the probability  $P(\varphi|\psi)$  of a state  $\varphi$  in a cage with fixed  $\psi$  is proportional to  $P^{\text{eq}}(\varphi)$  times the probability of having  $\psi$  in a cage. Thus  $P(\varphi|\psi) \propto P^{\text{eq}}(\varphi) \times \Omega_{\text{cage}}(\psi)/\Omega_{t_w}(\psi)$ , where  $\Omega_{\text{cage}}(\psi)$  is the number of states with  $\psi$  inside the cage, divided by the total number  $\Omega_{t_w}(\psi)$  of accessible states, not necessarily in the same cage, with  $\psi$ . Under the hypothesis of partial equilibrium  $S_{\text{cage}}(\psi) = \ln \Omega_{\text{cage}}(\psi)$  is the thermal equilibrium entropy in the cage.  $\Omega_{t_w}(\psi)$  depends on system age since more we wait more degrees of freedom relax.  $S_{t_w}(\psi) = \ln \Omega_{t_w}(\psi)$  is then smaller than the full thermodynamic entropy and converges to it only for  $t_w \gg t_{\text{eq}}$ . Using this ansatz for the PDF of the initial and final states, and the relation  $\partial S_{\text{cage}}(\psi)/\partial \psi = \beta h$  together with the analogous  $\partial S_{t_w}(\psi)/\partial \psi = x_{t_w} \beta h$ , corrected through the coefficient  $x_{t_w} < 1$  to account for the frozen degrees of freedom, we have  $\Delta S^{\text{eq}} - \Delta S_b = \beta h(\psi_t - \psi_{t_w}) - x_{t_w} \beta h(\psi_t - \psi_{t_w}) = (1 - x_{t_w}) \Delta S_{t_w, t}$ . Inserting this form into (6) the AFR (1) follows. The coefficient  $x_{t_w}$  measures the *phase space contraction* due to frozen degrees of freedom at  $t_w$ . Clearly  $x_{t_w} \rightarrow 1$  as  $t_w \gg t_{\text{eq}}$ .

**Numerical tests.** We have tested the AFR (1) through Monte Carlo simulations of several model systems, but we report results for only three of them. The system, initially prepared in an high temperature equilibrium state, is instantaneously quenched to a temperature  $T$  below the freezing transition temperature. After  $t_w$  a perturbation of small intensity, to ensure a good statistics for trajectories with  $\Delta S < 0$ , is applied and the fluctuations  $\Delta A_{t_w, t}$  of the conjugated variable  $A$  are recorded at fixed time intervals  $t - t_w$ . The maximum recording time  $t$  was taken much larger than  $t_w$  to ensure good statistics. The procedure was repeated several times,  $P_{t_w}(\Delta S)$  calculated from data binning and Eq.(1) tested to extract the value of  $x_{t_w}$ . To compare it with the parameter  $x = T/T_{\text{eff}}(t_w)$  obtained from the FDT, the fluctuation-dissipation (FD) plots in time-domain were also measured using the standard procedures [3]. Both  $x$  parameters (the one derived from the AFR, Eq.(1), and the one derived from FDT) asymptotically coincide under general assumptions, see [25].

The first model is the Random Orthogonal model (ROM) defined by the Hamiltonian [3]

$$\mathcal{H} = - \sum_{1 \leq i < j \leq N} J_{ij} \sigma_i \sigma_j, \quad (7)$$

where  $\sigma_i = \pm 1$  are Ising spins and  $J_{ij} = J_{ji}$  quenched Gaussian variables of zero mean and variance  $1/N$  satisfying  $\sum_k J_{ik} J_{kj} = 16 \delta_{ij}$ , with  $J_{ii} = 0$ . The system is perturbed by a uniform magnetic field of strength  $h$  conjugated to the total magnetization  $M(t) = \sum_i \sigma_i(t)$ .

This model describes structural glasses in the mode coupling theory (MCT) approximation and has a dy-

namical MCT transition at  $T_d = 0.536$ . Below  $T_d$  the system is dynamically confined into one of the many (exponentially large in number) metastable states and cannot reach full equilibrium. The equilibrium transition occurs at the lower static (or Kauzmann) temperature  $T_c = 0.25$ . The low-temperature behavior of the model is described by a one-step replica symmetry (1RSB) breaking order parameter. Typical signature of this is a two-slopes FD plot.

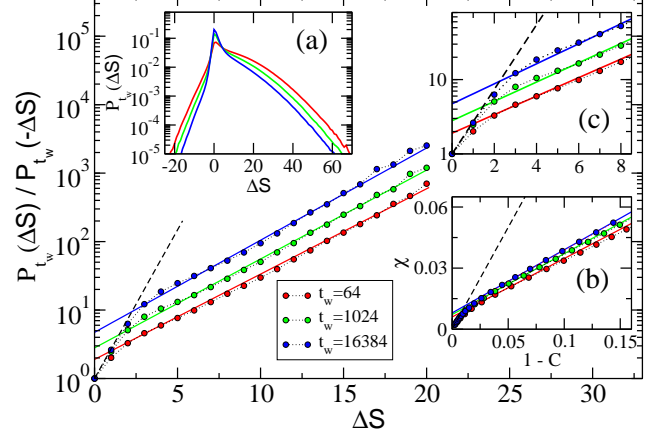


FIG. 1: **Numerical test of the AFR in the ROM.** Main plot is a test of Eq.(1) for the model with  $N = 1000$ ,  $T = 0.2$  and  $h = 0.1$  at three values of  $t_w$ . The dashed line corresponds to  $x_{t_w} = 1$  while full lines to  $x_{t_w} = 0.271, 0.287, 0.299$  for  $t_w = 64, 1024, 16384$  respectively. (a)  $P_{t_w}(\Delta S)$  and (b) FD plot. The dashed and continuous lines shown in the FD plot have slopes equal to those shown in the main plot. (c) Zoom of the region corresponding to  $x_{t_w} = 1$  (intra-cage relaxation).

Figure 1 shows results for the ROM. Two regimes can be distinguished,  $x_{t_w} = 1$  for  $|\Delta S| < \Delta S^*$  and  $x_{t_w} < 1$  for  $|\Delta S| > \Delta S^*$  ( $\Delta S^* \simeq 2$  for  $t_w = 1024$ ). The values of  $x_{t_w}$  agree quite well with  $x = T/T_{\text{eff}}$ , extracted from the FD plot [inset (b)].

As a more realistic system we have studied a 80 : 20 binary mixture of type  $A$  and  $B$  particles interacting via a Lennard-Jones pair potential (BMLJ):

$$V_{\alpha\beta}(r) = 4 \epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6 \right] \quad (8)$$

where  $\alpha, \beta = A, B$ ,  $r$  is the distance between the two particles and the parameters  $\sigma_{\alpha\beta}, \epsilon_{\alpha\beta}$  stand for the effective diameters and well depths between species  $\alpha, \beta$ . The parameters for length and energy measured in units of  $\sigma_{AA}$  and  $\epsilon_{AA}$  are  $\epsilon_{BB} = 0.5$ ,  $\epsilon_{AB} = 1.5$ ,  $\sigma_{BB} = 0.88$  and  $\sigma_{AB} = 0.80$ , and are taken to prevent crystallization [26]. With this choice a system of reduced density  $\rho = 1.2$  exhibits a glass transition well described by the MCT at the critical temperature  $T_{\text{MCT}} \simeq 0.435$ . The study of the AFR was done by adding at time  $t_w$  an external potential of the form  $V_0 \sum_j \epsilon_j \cos(\mathbf{k} \cdot \mathbf{r})$ , where  $V_0 < T$  and  $\epsilon_j$  are i.i.d. (quenched) random variables equal to  $\pm 1$  with

equal probability, and recording the conjugated observable  $A_k(t) = \sum_j \epsilon_j \exp[i\mathbf{k} \cdot \mathbf{r}_j(t)]$  [27]. Results for the AFR are shown, and compared with standard FD plots, in Fig 2. Also in this case the agreement between the  $x$  extracted from AFR and that from FD plot is rather good. Interestingly curves in the AFR plot do not exhibit the bending that can be seen in FD plots. Such bending is due to finite-size effects that for short  $t_w$  produce an equilibration of the system, and a depletion of the statistics of rare events for longer  $t_w$ . The plot then bends upward for short  $t_w$  and downward for longer  $t_w$ .

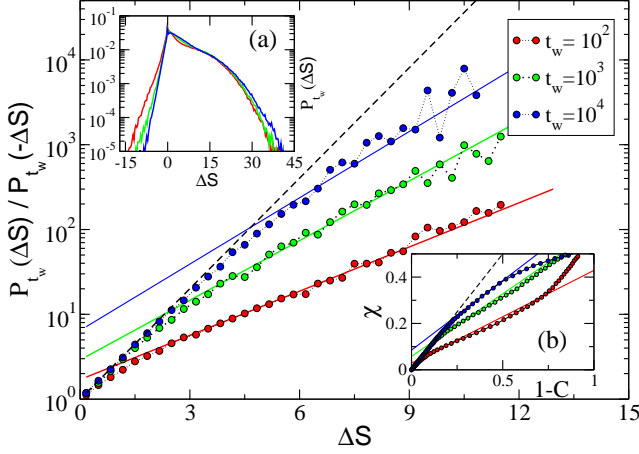


FIG. 2: **Numerical test of the AFR in the BMLJ model.** Main plot is a test of Eq.(1) for the model with parameters  $N = 500, V_0 = 0.1, |\mathbf{k}| = 7.25, T = 0.3$  at three values of  $t_w$ . The dashed line corresponds to  $x_{t_w} = 1$  while full lines (red, green, blue) to  $x_{t_w} = 0.40, 0.54, 0.60$  for  $t_w = 10^2, 10^3, 10^4$  respectively. (a)  $P_{t_w}(\Delta S)$  and (b) FD plot. The dashed and continuous lines (red, green, blue) in the FD plot have slopes equal to those shown in the main plot.

Both above systems are described by a two-steps relaxation, or 1RSB, scenario. As last example we have considered the 3-dimensional  $\pm J$  Edwards-Anderson model ( $\pm J$ -EA) defined by the Hamiltonian (7), but with  $J_{ij}$  randomly chosen equal to  $\pm 1$  if the sites  $j$  and  $i$  are nearest-neighbors on a cubic 3-dimensional lattice, and zero otherwise. Numerical investigation indicates that below  $T \simeq 1.14$  there is a spin-glass phase described by a continuous-step relaxation, or Full-RSB, scenario. Typical signature of this is a continuous-slope FD plot. Numerical tests of Eq.(1) for the  $\pm J$ -EA at two different  $t_w$  are shown in Fig.3, together with the FD plot. The AFR is well verified also in this model. However, as shown in inset (b) and in contrast to the previous 1RSB models, the phase contraction coefficient  $x_{t_w}$  agrees with  $T/T_{\text{eff}}$  only at the early stage, where the FD plot depart from equilibrium. This is in agreement with the aforementioned argument, according to which  $x_{t_w}$  gives information on the phase-space partition at  $t_w$ .

*Discussion.* Summarizing, the AFR (1) shows a promising route to experimentally test the *partial*

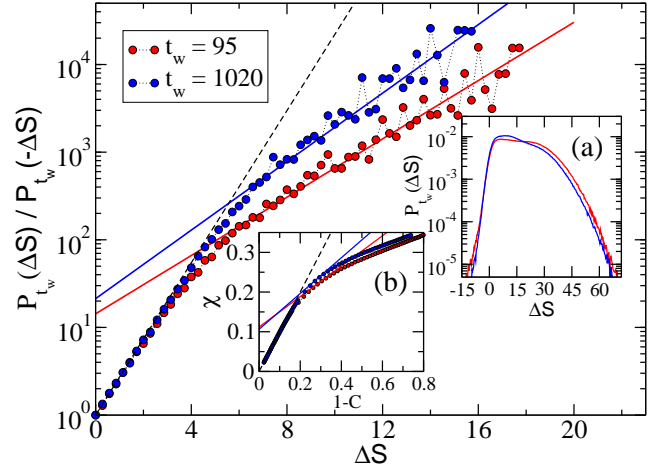


FIG. 3: **Numerical test of the AFR in the 3D  $\pm J$  EA model.** Main plot is a test of Eq.(1) for the model with parameters  $L = 16, T = 0.7$  and  $h = 0.1$  at two values of  $t_w$ . The dashed line corresponds to  $x_{t_w} = 1$  while full lines (red, blue) to  $x_{t_w} = 0.383, 0.450$  for  $t_w = 95, 1020$  respectively. (a)  $P_{t_w}(\Delta S)$  and (b) FD plot. The dashed and continuous lines (red, blue) in the FD plot have slopes equal to those shown in the main plot.

*equilibrium-entropy driven* scenario in slowly relaxing systems from noise measurements. A theoretical derivation of the AFR was given and its validity verified by extended numerical experiments. The connection between the values of  $x_{t_w}$  extracted from the AFR and FD plots was shown. Remarkably enough, and in contrast to FD plots, extracting the value of  $x_{t_w}$  does not require measuring aging correlation functions. By only measuring the statistics of  $\Delta S$  to an externally applied perturbation,  $P_{t_w}(\Delta S)$ , we can test the validity of Eq.(1) to extract the value of  $x_{t_w}$ . We emphasize that in order to test Eq.(1) statistical events with  $\Delta S < 0$  must be observed. Since the average value of  $\Delta S$  continuously increases with  $t$ , only rare events with  $\Delta S < 0$  give full meaning to the AFR. A similar situation is encountered in the Gallavotti-Cohen theorem for steady state systems [30]. Eq.(1) is ready to be employed in mesoscopic systems (e.g. magneto-conductance fluctuations in spin glasses and electron glasses [31, 32]) and single molecule experiments. The latter include molecular systems exhibiting slow folding due to disorder and frustration (e.g. RNA) or slow binding kinetics (e.g. peptides or proteins binding DNA). Ultimately, small systems may provide a direct access to experimentally measure the always elusive spin-glass order parameter.

AC thanks the LPTHE where part of this work was done. FR acknowledges support from HFSP Grant No. RGP55-2008, ICREA Academia 2008 and Spanish Research Council Grant. No. FIS2010-19342.



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- [1] J. P. Bouchaud, J. Phys. I (France) **2**, 1705 (1992)
- [2] L. F. Cugliandolo and J. Kurchan, Phil. Mag. B **71**, 501 (1995)
- [3] A. Crisanti and F. Ritort, Journal of Physics A (Math. Gen.) **36**, R181 (2003)
- [4] D. Hérisson and M. Ocio, Phys. Rev. Lett. **88**, 257202 (2002).
- [5] K. Komatsu *et al.*, Phys. Rev. Lett. **106**, 150603 (2011)
- [6] U. M. Bettolo-Marconi, A. Puglisi, L. Rondoni and A. Vulpiani, Phys. Rep. **461**, 111 (2008)
- [7] L. F. Cugliandolo, J. Kurchan and L. Peliti, Phys. Rev. E **55**, 3898 (1997)
- [8] R. G. Palmer, Adv. Phys. **31**, 669 (1982)
- [9] S. Franz and M. A. Virasoro, J. Phys. A **33** 891 (2000)
- [10] C. Jarzynski, Eur. Phys. J. B **64**, 331 (2008)
- [11] G.E. Crooks, Phys. Rev. E **61**, 2721 (1999)
- [12] F. Ritort, Advances in Chemical Physics, **137**, 31-123 (2008). Ed. Stuart. A. Rice, Wiley publications.
- [13] U. Seifert, Rep. Prog. Phys. **75**, 126001 (2012)
- [14] A. Alemany *et al.*, Nat. Phys. **8**, 688 (2012)
- [15] N. Kawashima and H. Rieger, *Frustrated Spin Systems*, p.491, Ed. H. Diep., World Scientific, Singapore (2005)
- [16] A. Crisanti and F. Ritort, Europhys. Lett. **66**, 253 (2004)
- [17] F. Ritort, *Unifying concepts in granular media and glassy systems*, p.129 Ed. by A. Coniglio, A. Fierro and H. Herrmann, Springer-Verlag, 2004.
- [18] J. R. Gomez-Solano, A. Petrosyan and S. Ciliberto, Phys. Rev. Lett. **106**, 200602 (2011)
- [19] L. Cugliandolo, D. Dean, J. Kurchan, Phys. Rev. Lett. **79**, 2168 (1997)
- [20] G. N. Bochkov and Y. E. Kuzolev, Sov. Phys. JEPT **45**, 125 (1977)
- [21] M. Campisi, P. Hanggi, and P. Talkner, Phil. Trans. R. Soc. A **369** 291-306 (2011)
- [22] E. Aurell *et al.*, Phys. Rev. Lett. **77**, 1262 (1996)
- [23] E. Aurell *et al.*, J. Phys. A **30**, 1 (1997)
- [24] U. Seifert, Phys. Rev. Lett. **95**, 040602 (2005)
- [25] See Supplemental Material at URL for a discussion.
- [26] W. Kob and H. C. Andersen, Phys. Rev. Lett. **73**, 1376 (1994)
- [27] J. L. Barrat and W. Kob, Europhys. Lett. **46**, 637 (1999)
- [28] B. Doliwa and A. Heuer, Phys. Rev. Lett. **91**, 235501 (2003)
- [29] Y. Yang and B. Chakraborty, Phys. Rev. E. **80**, 011501 (2009)
- [30] G. Gallavotti and E. D. G. Cohen, Phys. Rev. Lett. **74** 2694 (1995)
- [31] J. Jaroszynski *et al.*, Phys. Rev. Lett. **80** 5635 (1998)
- [32] D. Carpentier and E. Orignac, Phys. Rev. Lett. **100**, 057207 (2008)